

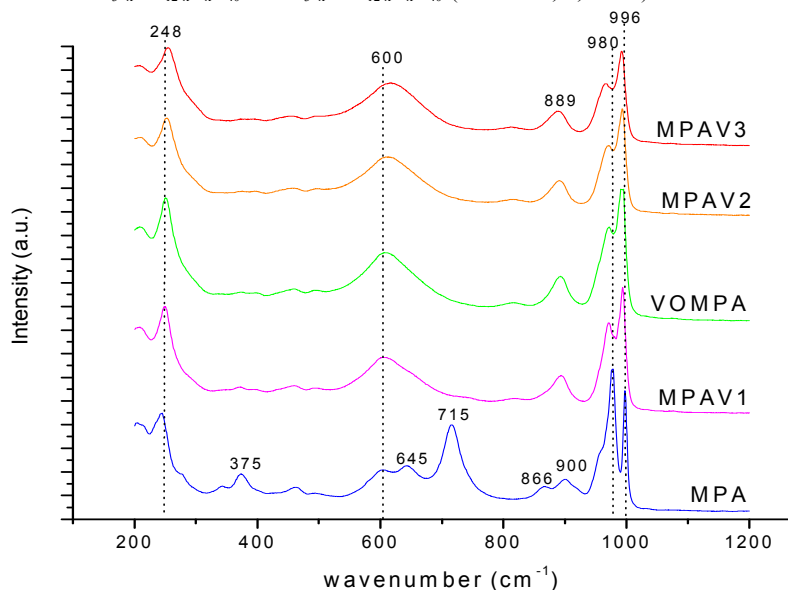
# Raman and UV-Vis Spectroscopy Study of Vanadium-Containing Heteropoly Acids in Aqueous Solutions

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## Introduction

To advance liquid phase spectroscopic techniques, we have selected two types of heteropoly acids (HPAs) in aqueous solutions to serve as our experimental catalysts:  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (TPA-tungstophosphoric acid) and  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  (MPA-molybdophosphoric acid). The cage-like structure that these HPAs assume is called the Keggin structure [1,2]. Distorted forms of the Keggin structure are also known to exist. For example, the Dawson structure is composed of two Keggin anions which have each expelled three  $\text{WO}_3$  or  $\text{MoO}_3$  units and joined together as a dimeric unit [1,3].

The initial objectives of this investigation were (1) to compare the ambient and aqueous solution spectra of the HPAs and (2) to determine differences or similarities in their structures between their ambient and aqueous states. Varying levels of vanadium were introduced into the primary and secondary structure of each HPA in order to investigate the influence of vanadium when the HPAs are in solution. TPA and MPA samples containing vanadium in the primary structure are denoted as TPAVx and MPAVx. The chemical formulas for solid TPAVx and MPAVx are  $\text{H}_{3+x}\text{PW}_{12-x}\text{V}_x\text{O}_{40}$  and  $\text{H}_{3+x}\text{PMo}_{12-x}\text{V}_x\text{O}_{40}$  (where  $x=1, 2$ , and 3). TPA and MPA



**Figure 1:** RT Raman spectra for 100 mM aqueous MPA, VOMPA, and MPAVx solutions.

which contain vanadia on the secondary structure are denoted as VOTPA and VOMPA.

## Materials and Methods

Solid powder TPA and MPA were purchased from Aldrich Chemical Co. The vanadium containing solid powder TPAs and MPAs were purchased from Nippon Inorganic Colour & Chemical Co. The VOTPA and VOMPA were prepared by depositing 1.5 moles of vanadia on 1 mole of either TPA or MPA.

Both solid state samples and aqueous solution samples at 100 mM concentrations of each HPA were examined at room temperature with Raman Spectroscopy (Horiba-Jobin Yvon LabRam-HR spectrometer; 532 nm). Solid state and aqueous solution samples at 0.5M concentrations were also examined with ambient UV-Vis spectroscopy (Varian Cary 5E) and evaluated using the Kubelka-Munk function [5]. The band gap energy or edge energy values ( $E_g$ ) and the ligand-to-metal charge transitions (LMCTs) for each sample were determined.

## Results and Discussion

The Raman spectra (shown in Figure 1 for the MPA series) exhibit the characteristic bands of the Keggin structure reported in the literature for both the aqueous and solid state hydrated samples [6], but the bands broaden as the vanadium content increases. This indicates that the Keggin structures remain intact in the aqueous solutions for TPA, TPAVx, VOTPA, MPAVx and VOMPA, and that the addition of vanadium causes the well-ordered Keggin structure to become somewhat disordered. The Raman spectrum for MPA in aqueous solution, however, displays an additional band at  $715\text{ cm}^{-1}$  (see Figure 1). This Raman band is characteristic of the Dawson structure [7] and indicates that the MPA Keggin structure in aqueous solution is unstable and breaks down to form a Dawson structure.

The  $E_g$  values for the HPAs were found to correlate with the total number of bridging bonds (V-O-Mo and V-O-W) indicating that the correlation published by Gao *et al.* is somewhat insensitive to type of neighboring metal atom in the second coordination sphere [8].

## Significance

In this study we have demonstrated that the Raman and UV-vis spectra of aqueous mixed metal oxides can be readily obtained. Comparison of the ambient and aqueous solution spectra reveals that the HPAs remain intact in aqueous environments. However, MPA transforms from the Keggin to the Dawson structure in aqueous solutions. These findings set the stage for spectroscopic characterization of aqueous solutions found during biocatalysis and biomass reforming.

## References

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